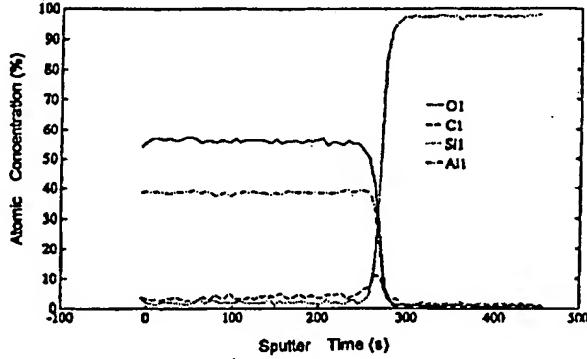


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 16/40		A1	(11) International Publication Number: WO 97/20963 (43) International Publication Date: 12 June 1997 (12.06.97)		
(21) International Application Number: PCT/KR96/00230		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).			
(22) International Filing Date: 3 December 1996 (03.12.96)		Published <i>With international search report.</i>			
(30) Priority Data: 1995-46455 4 December 1995 (04.12.95) KR					
(71) Applicant (for all designated States except US): KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY [KR/KR]; 100, Jang-dong, Yuseong-gu, Daejeon 305-343 (KR).					
(72) Inventors; and					
(75) Inventors/Applicants (for US only): KIM, Yun, Soo [KR/KR]; 383-11, Doryong-dong, Yuseong-gu, Daejeon 305-340 (KR). KOH, Won, Yong [KR/KR]; Kongdong Kwanri Apartment 8-302, 431, Doryong-dong, Yuseong-gu, Daejeon 305-340 (KR). KU, Su, Jin [KR/KR]; Posung Apartment 109-302, Wolsong-dong, Talso-gu, Taegu 704-400 (KR).					
(74) Agent: JANG, Seong, Ku; 275, Yangjae-dong, Seocho-gu, Seoul 137-130 (KR).					
(54) Title: PROCESS FOR THE PREPARATION OF ALUMINUM OXIDE FILM USING DIALKYLALUMINUM ALKOXIDE					
(57) Abstract					
An aluminum oxide film is economically and conveniently deposited on a substrate by a process which comprises vaporizing a dialkylaluminum alkoxide compound at a temperature ranging from 0 to 25 °C and contacting the resulting vapor with said substrate heated to a temperature ranging from 300 to 600 °C.					
					

BEST AVAILABLE COPY

- 1 -

PROCESS FOR THE PREPARATION OF ALUMINUM OXIDE FILM USING
DIALKYALUMINUM ALKOXIDE

Field of the Invention

5

The present invention relates to a process for coating a substrate with an aluminum oxide film by chemical vapor deposition using a dialkyaluminum alkoxide compound as an aluminum source.

10

Background of the Invention

There have hitherto been reported a number of chemical vapor deposition (CVD) methods for the preparation of an 15 aluminum oxide film. These methods are well summarized in recent review by E. Fredriksson et al., "Chemical Vapour Deposition of Aluminum Oxides from Various Gas Mixture," and J. Chemical Vapor Deposition, 1, 333-417 (1993) as well as in Korean translation of "CVD Handbook" pp 665-689 (Bando 20 Publishing Co., Seoul, Korea, 1993). Aluminum trichloride and triisopropoxide have been most commonly used as aluminum sources in the CVD of an aluminum oxide film due to their low cost and ready availability. These conventional aluminum sources have low vapor pressures and are usually 25 heated to higher than 100 °C to generate a vapor stream to be used in a CVD process.

Further, trialkylaluminums have been used in the CVD of an aluminum oxide film, which are liquid at room temperature

- 2 -

and have relatively high vapor pressure. However, such trialkylaluminums do not contain oxygen atoms, thus the use of an oxygen source such as O₂ or N₂O is essential for the formation of an aluminum oxide film. Also trialkylaluminums 5 are pyrophoric when exposed to air. U.S. Patent No. 4,675,089 discloses a plasma-assisted CVD method of depositing an amorphous thin film of aluminum oxide using a trialkylaluminum vapor and carbon dioxide. However, this method requires expensive equipments to produce plasma and 10 have lower throughput compared to a thermal CVD method, thus less suitable for use in a large-scale application.

Summary of the Invention

15 Accordingly, it is an object of the present invention to provide an efficient and economical process for the preparation of an aluminum oxide film suitable for a large-scale production of articles coated with aluminum oxide film.

20 In accordance with one aspect of the present invention, there is provided a process for coating a substrate with an aluminum oxide film, which comprises contacting a vaporized dialkylaluminum alkoxide compound with said substrate heated to a temperature ranging from 300 to 600 °C.

25

Brief Description of the Drawings

FIG. 1 represents an Auger electron spectrum of an

- 3 -

aluminum oxide film deposited on Si(100) at 400 °C using diethylaluminum isopropoxide in accordance with Example 6 of the present invention; and

FIG. 2 shows an Auger depth profile of the film 5 obtained in Example 6.

Detailed Description of the Invention

The present invention is characterized in that a 10 dialkylaluminum alkoxide is used as an aluminum source in the chemical deposition of an aluminum oxide film.

The dialkylaluminum alkoxide useful for practicing the present invention is a material which has a high vapor pressure sufficient to vaporize under an ambient condition, 15 i.e., 0.06 to 0.5 mmHg at a temperature ranging from 0 to 25 °C. The dialkylaluminum alkoxide compound suitable for use in the present invention is represented by the following formula:



20 wherein R¹ and R² are each independently a C₁₋₁₀ alkyl group.

The dialkylaluminum alkoxide compound according to the present invention may be prepared by reacting an alkylaluminum with an alcohol at a low temperature by a conventional method, e.g., as is described by Paul S. Coan, 25 et al. in Organometallics, 8, 2724 (1989), or by reacting an alkylaluminum with an aluminum alkoxide in a molar ratio of 2:1 at room temperature.

The preferred dialkylaluminum alkoxide compound in

- 4 -

practicing the present invention may be dimethylaluminum isopropoxide, diethylaluminum isopropoxide, dimethylaluminum *t*-butoxide and a mixture thereof. Under an ambient condition, dimethylaluminum isopropoxide is a liquid, 5 whereas diethylaluminum isopropoxide and dimethylaluminum *t*-butoxide are gel-like solids.

In accordance with the present invention, the dialkylaluminum alkoxide compound is vaporized at an ambient temperature ranging from 0 to 20 °C and the vapor thereof is 10 then contacted with the surface of a substrate heated at a temperature ranging from 300 to 600 °C to deposit an aluminum oxide film thereon.

The vaporization of dialkylaluminum alkoxide compound may be carried out in a reactor which is preferably 15 maintained at an internal pressure of 10 to 50 mbar.

The substrate which may be used in practicing the present invention is an inorganic solid which is stable under the CVD condition and examples thereof include glass, quartz, silicon, gallium arsenide, sapphire, alkali metal 20 niobate, alkaline earth metal titanate, gallium nitride, niobium nitride and the like, among which silicon single crystal is preferred when the coated substrate is intended for electronic applications.

The following Preparatives and Examples are provided 25 for the purposes of illustrating certain aspects of the present invention only; they are not to be construed as limiting the scope of the present invention in any way.

- 5 -

Preparative 1: Synthesis of dimethylaluminum t-butoxide

To 2.07 g (28.7 mmol) of trimethyl aluminum dissolved in 30 ml of dry ethyl ether was added 2.13 g (28.7 mmol) of 5 t-butanol at -70 °C, and the resulting mixture was warmed to room temperature while stirring and the solvent was evaporated off under a reduced pressure. The residue was sublimed to obtain 2.16 g (16.6 mmol, 58 % yield) of the title compound in the form of a gel-like solid. ¹H NMR 10 analysis in benzene-d₆ of the compound obtained showed peaks at δ -0.42(s, Al(CH₃)₂, 6H) and 1.15(s, OC(CH₃)₃, 9H).

Preparative 2: Synthesis of dimethylaluminum isopropoxide

15 To 2.75 g (38.1 mmol) of trimethyl aluminum was added 3.90 g (19.1 mmol) of aluminum isopropoxide which was previously purified by distillation under a reduced pressure to obtain 12.52 g (108 mmol, 87 % yield) of the title compound in the form of a colorless liquid that boils at a 20 temperature ranging from 68 to 72 °C at 10 mmHg. ¹H NMR in benzene-d₆ analysis of the compound obtained showed peaks at δ -0.47(s, Al(CH₃)₂, 6H), 0.99(d, OCH(CH₃)₂, 6H) and 3.84(heptet, OCH(CH₃)₂, 1H).

25 Preparative 3: Synthesis of diethylaluminum isopropoxide

To 1.21 g (10.6 mmol) of triethyl aluminum (93 % purity, Aldrich Chemical Co.) was added 1.08 g (5.3 mmol) of

- 6 -

aluminum triisopropoxide which was previously purified by distillation under a reduced pressure, and the resulting mixture was stirred for 24 hours and the mixture was sublimed to obtain 1.89 g (13.5 mmol, 85 yield as 5 diethylaluminum isopropamide) of the title compound in the form of a gel-like solid.

Example 1

10 0.05 g of dimethylaluminum *t*-butoxide prepared in Preparative 1 was vaporized at 0 °C and the vapor thereof was conveyed to a Si(100) substrate preheated to 400 °C to conduct the chemical vapor deposition for 3 hours. The X-ray photoelectron spectrum of the deposited film showed 15 peaks corresponding to oxygen and aluminum as well as carbon, but not the peaks for silicon. This observation shows that the surface of the silicon substrate is completely covered by an aluminum oxide film.

20 Example 2

The procedure of Example 1 was repeated except that the Si(100) substrate was preheated to 300 °C and the chemical vapor deposition was carried out for 1 hour. The X-ray 25 photoelectron spectrum of the deposited film showed peaks corresponding to oxygen and aluminum as well as carbon, but not the peaks for silicon.

- 7 -

Example 3

0.1 g of dimethylaluminum isopropoxide prepared in Preparative 2 was vaporized at room temperature and the 5 vapor thereof was transported to a Si(100) substrate preheated to 350 °C to conduct the chemical vapor deposition for 5 hours. The X-ray photoelectron spectrum of the deposited film showed peaks corresponding to oxygen and aluminum as well as carbon, but not the peaks for silicon.

10

Example 4

0.1 g of diethylaluminum isopropoxide prepared in Preparative 3 was vaporized at room temperature and the 15 vapor thereof was brought into contact with a Si(100) substrate preheated to 350 °C to conduct the chemical vapor deposition for 2 hours. The X-ray photoelectron spectrum of the deposited film showed peaks corresponding to oxygen and aluminum as well as carbon, but not the peaks for silicon.

20

Example 5

0.1 g of dimethylaluminum isopropoxide prepared in Preparative 2 was vaporized at room temperature and the 25 vapor thereof was carried to a Si(100) substrate preheated to 600 °C to conduct the chemical vapor deposition for 5 hours. The X-ray photoelectron spectrum of the deposited film showed peaks corresponding to oxygen and aluminum as

- 8 -

well as carbon, but not the peaks for silicon.

Example 6

5 0.1 g of diethylaluminum isopropoxide prepared in
Preparative 3 was vaporized at room temperature and the
vapor thereof was transported to a Si(100) substrate
preheated to 400 °C to conduct the chemical vapor deposition
for 10 hours. The Auger electron spectrum of the deposited
10 film obtained after sputtering for 6 seconds with 3.5 keV
Ar⁺ ion beam is shown in FIG. 1. And Auger depth profile of
the same film is shown in FIG. 2.

These data clearly indicate that the film is
stoichiometric with no appreciable carbon incorporation and
15 the composition is constant through the bulk of the film.

The thickness of the aluminum oxide film is estimated
at 0.23 μm, assuming an etch rate of 0.83 nm/s.

In accordance with the present invention as described
20 above, an aluminum oxide film can be conveniently and
effectively deposited on a substrate by way of using a
dialkylaluminum alkoxide compound as an aluminum source.
The inventive process has the advantage that gas phase
mixing can be completely avoided because no additional
25 oxygen source is necessary, thus a large-scale production of
aluminum oxide films is possible using simple equipments
under much simplified conditions.

- 9 -

While the invention has been described with respect to the specific embodiments, it should be recognized that various modifications and changes may be made by those skilled in the art to the invention which also fall within 5 the scope of the invention as defined by the appended claims.

- 10 -

What is claimed is:

1. A process for coating a substrate with an aluminum oxide film, which comprises contacting a vaporized 5 dialkylaluminum alkoxide compound of formula (I) with said substrate:



wherein R^1 and R^2 are each independently a C_{1-10} alkyl group.

10 2. The process of claim 1 wherein the substrate is heated to a temperature ranging from 300 to 600 °C.

15 3. The process of claim 1 wherein the vaporization of dialkylaluminum alkoxide compound is conducted at a temperature ranging from 0 to 25 °C.

4. The process of claim 2 wherein the dialkylaluminum alkoxide compound is selected from the group consisting of dimethylaluminum isopropoxide, diethylaluminum isopropoxide, 20 dimethylaluminum t-butoxide and a mixture thereof.

5. The process of claim 4 wherein the dialkylaluminum alkoxide compound is dimethylaluminum isopropoxide.

25 6. The process of claim 1 wherein the substrate is a silicon single crystal.

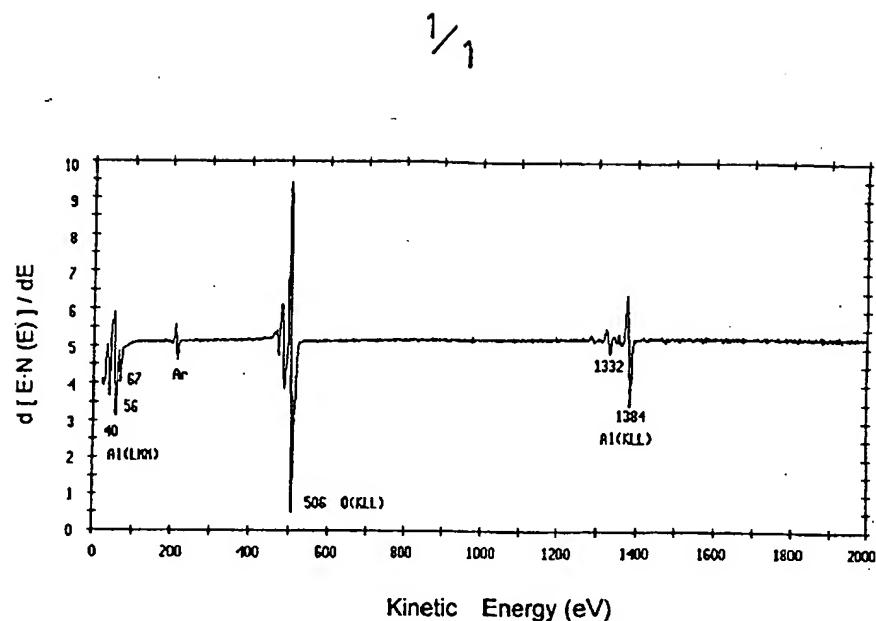


FIG. 1

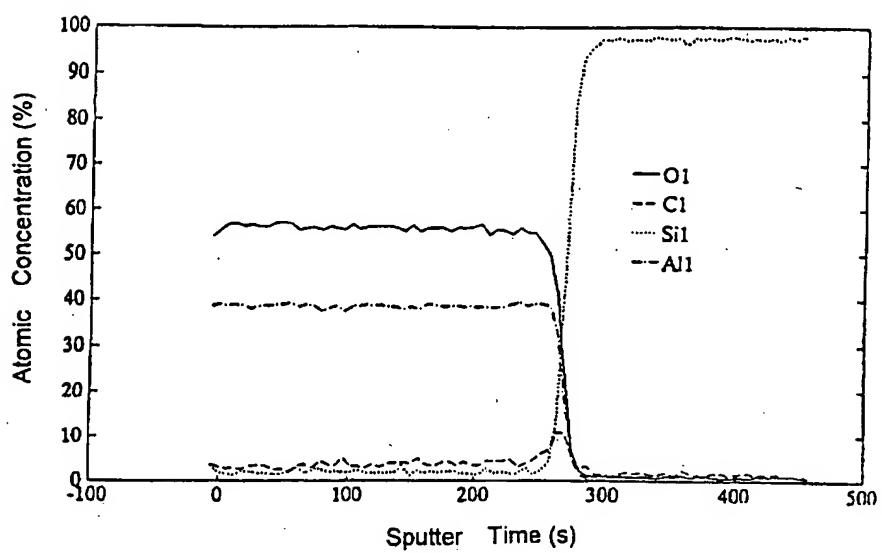


FIG.2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 96/00230

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 23 C 16/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 23 C 16/40, 16/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 460 254 A1 (SCHERING AKTIENGESELLSCHAFT) 11 December 1991 (11.12.91), abstract; page 2, line 55; page 3, lines 31-32; example 6; claims 1-14.	1-6
X	DE 39 18 932 A1 (SCHERING AKTIENGESELLSCHAFT) 13 December 1990 (13.12.90), abstract; column 2, line 31; column 3, lines 15-17; claims 1-14.	1-6
A	GB 2 202 865 A (THE PLESSEY COMPANY PLC) 05 October 1988 (05.10.88), abstract; claims 1-9.	1-6
A	US 5 389 401 A (ROY G. GORDON) 14 February 1995 (14.02.95), abstract; claims 1-12.	1-6

<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
--------------------------	--	--------------------------	--------------------------

<ul style="list-style-type: none"> • Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed 	<ul style="list-style-type: none"> “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family
---	--

Date of the actual completion of the international search	Date of mailing of the international search report
06 February 1997 (06.02.97)	18 February 1997 (18.02.97)
Name and mailing address of the ISA/ AT AUSTRIAN PATENT OFFICE Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/535	Authorized officer Hauk Telephone No. 1/53424/217

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 96/00230

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la familie de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1 450254	11-12-91	CA AA 2018464 DD A5 294974 DE A1 3918932 JP A2 3111574	08-12-90 17-10-91 13-12-90 13-05-91
DE A1 3918932	13-12-90	CA AA 2018464 DD A5 294974 JP A2 3111574 EP A1 450254	08-12-90 17-10-91 13-05-91 11-12-91
GB A 2202865		EP A1 307444 GB A0 870773 GB A1 2202865 IL A0 880587 JP T2 1507151 US A 5045348 WO A1 8807739 ZA A 8802160	22-03-89 09-04-87 05-10-86 02-09-86 02-10-81 02-09-80 06-10-80 26-04-80
US A 5389401	14-02-95	Keine - none - rien	

BEST AVAILABLE COPY